Probing Forbidden Low-Frequency Raman Modes in MoS_2 via Plasmonic Nanoparticle

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1. Introduction

Interlayer interaction through the van der Waals forces in two-dimensional (2D) materials like molybdenum disulfide (MoS_2) determine most of the layer properties, which shows up as low-frequency modes (less than 50cm^{-1}) in Raman scattering. But the weak low-frequency signals are often obscured by background noise, requiring enhancement techniques [1]. Furthermore, detecting forbidden low-frequency Raman modes poses additional challenges. These modes, suppressed by symmetry selection rules, provide important information into molecular structures and electronic properties but are not observed in conventional Raman spectroscopy as they are symmetry forbidden. Our approach can detect forbidden low-frequency modes and achieve high-sensitivity through low-frequency surface-enhanced Raman spectroscopy (LF-SERS).

2. Result and discussion

We utilize silver nanoparticles to detect forbidden low-frequency Raman modes in MoS_2 by breaking the selection rules. The strong gradient of near-field light with sharply varying intensity within a nanometric volume near the nanoparticle causes selective symmetry breaking as shown in Fig.1. This breaks the Raman selection rules, allowing the observation of vibration patterns that are forbidden in Raman spectroscopy [2].

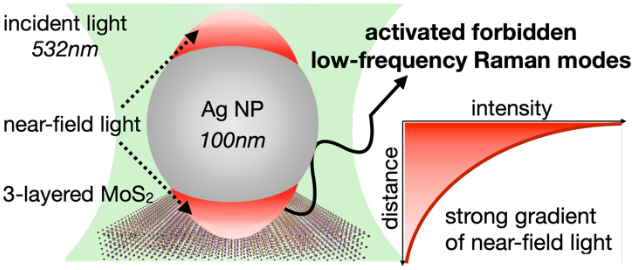

Figure 1. Gradient near-field light in the vicinity of a nanoparticle.

We used 3-layered MoS_2 as the sample and placed silver nanoparticles on its surface. We measured a LF-SERS image constructed with its breathing and shear modes at 28 cm^{-1} and observed high-intensity Raman signals only around the nanoparticle, as shown by the bright areas in Fig. 2(a). MoS_2 has four vibration modes in the low-frequency range: the breathing and the shear modes, both appearing at 28 cm^{-1}, are Raman-active, while the E" (15 cm^{-1}) and A_2" (46 cm^{-1}) modes are forbidden in Raman scattering. The forbidden Raman modes can only be activated near an isolated single particle as seen in Fig. 2(b). An AFM image and a SERS image from one of the isolated single particles are shown in Figs. 2(c) and 2(d), respectively. We demonstrate how LF-SERS changes with the gradient near-field light around this nanoparticle, which are measured from the points marked in Fig. 2(d). The forbidden Raman modes only appear in region with a strong gradient, as shown in the spectrum by the blue areas in Fig.2(e).

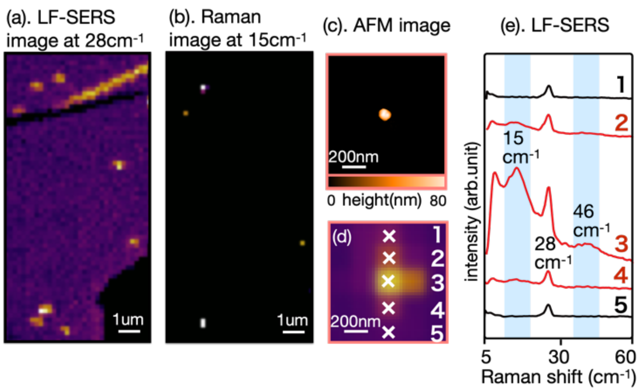

Figure 2. Forbidden LF-SERS image and spectrum.

To confirm our experimental results, we used calculations based on the density functional theory (DFT) to simulate Raman spectrum of a 3-layered MoS_2. Our simulations confirm the existence of forbidden Raman modes in MoS_2, with the vibration modes calculated by DFT matching the two forbidden Raman peaks detected in our experiments. Without the silver nanoparticles, these vibration modes are present but have zero intensity, indicating they are Raman-forbidden. The DFT calculations further reveal that the activation of these modes is not only due to the strong gradient near-field light but also involves physical contact deformation and charge transfer between the MoS_2 and the silver nanoparticles.

3. Conclusions

Our technique enables the first observation of LF-SERS and plasmonically activated forbidden low-frequency Raman modes in MoS_2, providing more information into the material's vibrational properties and advancing material characterization methods.

References

[1] P. Verma et al., Sci Rep 10, 21227 (2020).
[2] K. Ikeda et al., J. Am. Chem. Soc. 135 (2013).